



TITLE:

Novel π -Conjugated Systems: The First Silatropylium Ion and Planar Cyclooctatetraene Annelated with Bicyclic Frameworks and New Derivatives of Fullerene C60 (ORGANIC MATERIALS CHEMISTRY-High-Pressure Organic Chemistry)

AUTHOR(S):

Komatsu, Koichi; Nishinaga, Tohru; Murata, Yasujiro; Matsuura, Akira; Izukawa, Yoshiteru; Kato, Noriyuki

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Novel π -Conjugated Systems: The First Silatropylium Ion and Planar Cyclooctatetraene Annelated with Bicyclic Frameworks and New Derivatives of Fullerene C₆₀

Koichi Komatsu, Tohru Nishinaga, Yasujiro Murata, Akira Matsuura,
Yoshiteru Izukawa, and Noriyuki Kato

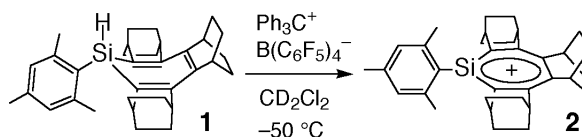
The first silylium ion with cyclic π -conjugation, the silatropylium ion, was prepared, which was made possible by annelation with three bicyclo[2.2.2]octene frameworks and steric protection of the silylium-ion center by a mesityl group. The presence of cyclic π -conjugation through the p-orbital of silicon was confirmed by NMR measurements. The first planar cyclooctatetraene was synthesized by cuprate mediated cyclotetramerization of 2,3-diiodobicyclo[2.1.1]hexene, and its structure determined by X-ray crystallography. On the other hand, a thermal reaction of fullerene C₆₀ with phthalazine in solution afforded a C₆₀ derivative with an eight-membered-ring opening on the surface while the reaction conducted in the solid state gave a novel adduct with two C₆₀ cages incorporated in a bicyclic framework.

Keywords: silylium ion / Hückel aromaticity / cyclooctatetraene / fullerene / rearrangement

1. The First Silatropylium Ion^[1] and Planar Cyclooctatetraene^[2] Stabilized by Bicycloannellation.

The problem of generation or isolation of the silyl cation in the condensed phase has been among the central issues of organosilicon chemistry. So far the reports on a silylium ion having no coordination with the solvent or counteranion are quite limited. Furthermore, there has been no example on the silylium ion incorporated in cyclic π -conjugation. As one of such π -conjugated silylium ions, the silatropylium ion is of great interest, but its presence either in solution or in gas phase has been highly questioned from the theoretical viewpoint.

In the present study, the first silatropylium ion was made possible by applying the annelation with rigid bicyclic frameworks and the protection of the silicon atom by the sterically demanding mesityl group.



Thus the hydride abstraction from mesitylsilacycloheptatriene **1** in CH_2Cl_2 at low temperature successfully afforded the silatropylium ion **2**, which was confirmed by NMR measurements. In cation **2** the ^{29}Si NMR signal (δ 142.9) was downfield shifted from **1** by 192.2 ppm, and so were the ^{13}C NMR signals for the seven-membered ring carbons. Furthermore, the down-field shift of the ^1H NMR signals of the bridgehead protons of the bicyclic frameworks indicated the presence of a diamagnetic ring current. Thus, the silatropylium ion **2** is con-

ORGANIC MATERIALS CHEMISTRY — High-Pressure Organic Chemistry —

Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic π -systems having σ - π conjugation; synthesis of redox-active dehydroannulenes; chemical transformation of fullerene C₆₀; mechanochemical reactions of fullerenes.



Prof
KOMATSU
Koichi
(D Eng)



Instr
MORI
Sadayuki
(D Eng)



Instr
NISHINAGA
Tohru
(D Eng)



Instr
MURATA
Yasujiro
(D Eng)

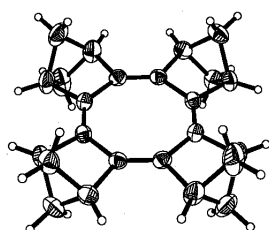
Students:

MATSUURA, Akira (DC)
FUJIWARA, Koichi (DC)
WAKAMIYA, Atsushi (DC)
ITO, Miho (MC)
NODERA, Nobutake (MC)
INOUE, Ryouta (MC)
SUZUKI, Mitsuharu (MC)
MURATA, Michihisa (UG)
YAMAZAKI, Daisuke (UG)

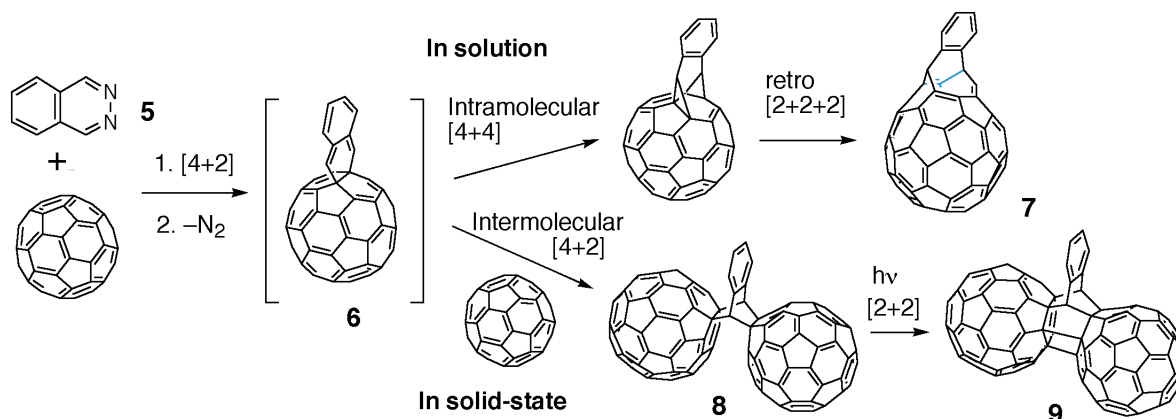
sidered as a new example of a positively charged aromatic π -conjugated system containing silicon.

Cyclooctatetraene (COT) is known as a tub-shaped molecule. However, annelation with a highly strained system such as bicyclo[2.1.1]hexene (BCH) is expected to cause planarization of the COT ring, which is of great interest from the viewpoint of antiaromaticity and realization of a novel electronic structure.

When 2,3-diiodobicyclo[2.1.1]hexene was monolithiated and treated with CuI, the COT **4** annelated with four BCH units was obtained in 21% yield together with benzene **3** in 34% yield. The structure of novel COT **4** was determined by X-ray crystallography: **4** has a completely planar eight-membered ring with remarkable bond alternation (1.331 Å and 1.500 Å with the shorter bonds exocyclic to bicycloannellation). The planarization of the COT ring in **4** results in elevation of a HOMO level and reduction of HOMO-LUMO gap as shown by the long-wavelength absorption (459 nm) and extremely low oxidation potentials ($E_{1/2}(1)$ +0.07 V vs Fc/Fc⁺, $E_{pa}(2)$ +0.76 V). The antiaromaticity in COT **4** is greatly reduced due to the bond alternation and also σ - π interaction.



X-ray structure of COT **4**



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